*R* factor of 0.056. After calculated H positions of the phenyl groups and solvent molecule were added to the atomic coordinate list, a subsequent difference-Fourier map revealed the seven H positions of the [B$_2$H$_7$]$^-$ anion. Exhaustive least-squares refinement (in which the H coordinates of the anion were also varied) resulted in a final *R* factor of 0.049 for 3569 nonzero reflections [*I* > 3σ(*I*)].[9]

A plot of the [B$_2$H$_7$]$^-$ anion is shown in Figure 1, and selected distances and angles are given in Table I. Other results of the structural analysis are available.[10] The single-H-bridged model is confirmed, with a bent B–H–B linkage [136 (4)°]. The terminal H atoms are found in staggered arrangement, and the molecular conformation has C_s symmetry, as depicted in I. (This confor-

I
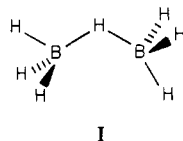
mation can be seen in Figure 1: note the approximate mirror plane defined by the atoms H$_3$, B$_1$, H$_1$, B$_2$, H$_5$, which are coplanar within ±0.03 Å). As expected for an X-ray analysis, the individual B–H distances show considerable scatter (Table I), but the average terminal B–H distance (1.03 Å) is appreciably shorter than the average bridging B–H distance (1.14 Å), as anticipated. The apparent asymmetrical positioning of the bridging H atom [B$_1$ – H$_1$ = 1.27 (5) Å, B$_2$ – H$_1$ = 1.00 (5) Å] may reflect some sort of donor–acceptor interaction (i.e., BH$_4^-$ → BH$_3$), but until more accurate H positions are available (hopefully, from a neutron diffraction analysis[11]), we cannot be sure if this phenomenon is real. The B···B distance of 2.107 (7) Å is very much shorter than the corresponding distance found in [B$_2$(C$_4$H$_8$)$_2$H$_3$]$^-$ (B···B = 2.43 Å), and this is probably a consequence of the removal of steric constraints (i.e., the two C$_4$H$_8$ bridges) in going from [B$_2$(C$_4$-H$_8$)$_2$H$_3$]$^-$ to [B$_2$H$_7$]$^-$.

We have now completed the structural analysis of the entire sequence of compounds having unsupported X–H–X bonds,[2] i.e., compounds having M–H–M, M–H–B, and B–H–B linkages. The M–H–M class is represented by our neutron diffraction studies of several compounds having single W–H–W bridges,[12] and the M–H–B class by our recent neutron analysis of (Ph$_2$MeP)$_3$Cu-(BH$_4$).[13] All these investigations have shown the existence of bent 3-center two-electron linkages, consistent with the present structural results on [B$_2$H$_7$]$^-$. On the other hand, a recent X-ray study of [Me$_3$Al(μ-H)AlMe$_3$]$^-$ revealed a linear Al–H–Al bond.[14] In order to check out the possibility that the conformation of [B$_2$H$_7$]$^-$ might be sensitive to crystal lattice effects,[15] we are

planning to carry out the structure analyses of other salts of this anion.[16]

---

(16) The X-ray diffraction analysis of [Ph$_3$MeP]$^+$[B$_2$H$_7$]$^-$ is currently, being attempted (Chiang, M.; Bau, R.; Lawrence, S. H.; Shore, S. G.).

A [4 + 4] Annulation Approach to Eight-Membered Carbocyclic Compounds[1a]

Rick L. Danheiser,*[1b] Stephen K. Gee, and Howard Sard

*Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*

Received August 23, 1982

Although cyclooctane derivatives have been the subject of extensive physical-organic investigations, relatively little progress has been made toward the development of general synthetic approaches to this system. The recent isolation of a number of biologically important natural products whose structures incorporate eight-membered rings has lent further importance to the search for new methodology for the synthesis of cyclooctane derivatives. Cyclooctane derivatives are most commonly prepared either by cyclization methods, via the ring expansion of cycloheptanes, or by the cleavage (or fragmentation) of bi- and polycyclic systems that already incorporate eight-membered rings. Few general annulation[2] approaches to cyclooctanes have been described previously. 1,5-Cyclooctadienes can be prepared via the thermal,[3] photochemical,[4] or nickel(0)-catalyzed[5] dimerization of 1,3-dienes, followed by Cope rearrangement of the intermediate 1,2-vinylcyclobutanes. Unfortunately this [4 + 4] annulation process generally proceeds in low yield and is both nonstereoselective and regiochemically ambiguous.

In this communication we describe a new [4 + 4] annulation approach to eight-membered carbocycles that is applicable to the synthesis of unsymmetrically substituted and highly functionalized cyclooctane derivatives. As outlined in Scheme I, 1,3-dienes serve as one four-carbon component in this annulation. The second four-carbon unit is a vinylketene derivative, generated either by electrocyclic opening of a cyclobutenone or via the 1,4-dehydrohalogenation of an α,β-unsaturated acid chloride.

The cyclobutenone version of the annulation simply involves heating the enone and 1,3-diene in an inert solvent and proceeds via a cascade of well-precedented pericyclic reactions (one representing each major class of pericyclic process!). Electrocyclic opening of the cyclobutenone[6] generates a vinylketene derivative

(9) Major computations in this work were performed on the USC IBM 370/158 computer using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

(10) See supplementary material paragraph at end of paper.

(11) A neutron diffraction analysis was in fact attempted on [(Ph$_3$P)$_2$N]$^+$[B$_2$H$_7$]$^-$·CH$_2$Cl$_2$ very recently (Chiang, M.; Koetzle, T. F.; Bau, R.; Shore, S. G.; Lawrence, S. H., July 1982), but the size of the crystal used in that work was not large enough to yield a satisfactory data set. Efforts are continuing.
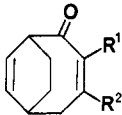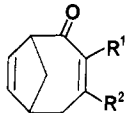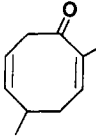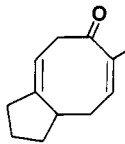
(12) (a) HW$_2$(CO)$_9$(NO): Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M. A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 6621. (b) HW$_2$(CO)$_8$(NO)P(OMe)$_3$: Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey, B. R.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4491. (c) [Et$_4$N]$^+$[NW$_2$(CO)$_{10}$]$^-$ and [Ph$_4$P]$^+$[HW$_2$(CO)$_{10}$]$^-$: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

(13) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C. Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165.

(14) Atwood, J. L.; Hrncir, D. C.; Rogers, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6787.

(15) In this regard, it should be noted that there is some precedence for conformational changes due to crystal packing forces. For example, the non-hydrogen skeleton of the [HW$_2$(CO)$_{10}$]$^-$ anion is linear and eclipsed in [Et$_4$N]$^+$[HW$_2$(CO)$_{10}$]$^-$ but bent and staggered in [(Ph$_3$P)$_2$N]$^+$[HW$_2$(CO)$_{10}$]$^-$ (Wilson, R. D.; Graham, S. A.; Bau, R. *J. Organomet. Chem.* **1975**, *91*, C49). Nevertheless, the W–H–W core is bent in all salts of [HW$_2$(CO)$_{10}$]$^-$ investigated so far, including [Et$_4$N]$^+$[HW$_2$(CO)$_{10}$]$^-$ (see Figure 4 in ref 12c).

(1) (a) Presented at the 183rd National Meeting of the American Chemical Society, March 30, 1982; (b) Alfred P. Sloan Research Fellow, 1981–1983.

(2) We define as annulations those ring-forming processes in which *two* molecular fragments are united with the formation of *two* new bonds.

(3) (a) Cope, A. C.; Schmitz, W. R. *J. Am. Chem. Soc.* **1950**, *72*, 3056. (b) Vogel, E. *Justus Liebigs Ann. Chem.* **1958** *615*, 1. (c) Sartori, G.; Turba, V.; Valvassori, A.; Riva, M. *Tetrahedron Lett.* **1966**, 4777. (d) Stewart, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 4815. (e) Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *Ibid.* **1976**, *98*, 5937 and references cited therein.

(4) (a) Hammond, G. S.; De Boer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899. (b) Trecker, D. J.; Henry, J. P. *Ibid.* **1964**, *86*, 902 and references cited therein.

(5) For a review, see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Wiley: New York, 1975; Vol. II, Chapter 4.

Communications to the Editor

J. Am. Chem. Soc., Vol. 104, No. 26, 1982 7671

Table I. [4 + 4] Annulations

diene	vinylketene precursor	annulation product	yield,[a,b] %
1,3-cyclohexadiene	3	6, R^1 = H; R^2 = CH$_3$	49[c]
1,3-cyclohexadiene	4	7, R^1 = H; R^2 = n-Bu	33[c]
1,3-cyclohexadiene	5	8, R^1 = R^2 = CH$_3$	91[c]
1,3-cyclohexadiene	tigloyl chloride	11, R^1 = CH$_3$; R^2 = H	31[d]
1,3-cyclohexadiene	2-chloro-2-butenoyl chloride	14, R^1 = Cl; R^2 = H	44[d]
cyclopentadiene	crotonyl chloride	9, R^1 = R^2 = H	18[d]
cyclopentadiene	tigloyl chloride	10, R^1 = CH$_3$; R^2 = H	40[d]
(E)-1,3-pentadiene	tigloyl chloride	**12**	30,[d] 25[c]
1-vinylcyclopentene	tigloyl chloride	**13**	19[c]

[a] Overall isolated yields of purified products, based on cyclobutenone or acyl chloride. [b] See ref 12. [c] One-step annulations. For **12**: CHCl$_3$, 137 °C, 2 h. For **13**: cyclohexane, 100 °C, 41 h. [d] The intermediate divinylcyclobutanone(s) were isolated and purified prior to Cope rearrangement. For **9-11**, see text. For **12**: [2 + 2] cycloaddition (CHCl$_3$, 73 °C, 19 h) gave **12** (16%) + **21** (34%); further thermolysis of **21** was then effected in toluene (150 °C, 45 min). For **14**: [2 + 2] cycloaddition carried out in cyclohexane (80 °C, 21 h), then further thermolysis in cyclohexane (140 °C, 2 h).

Scheme I
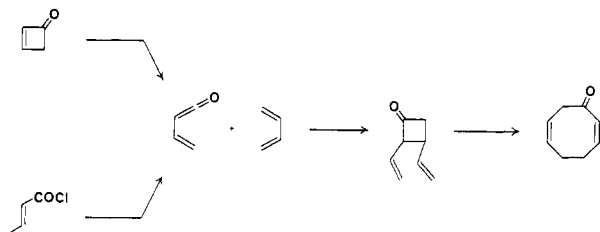
that combines with the conjugated diene in a regiospecific [2 + 2] cycloaddition.[7,8] At the elevated reaction temperature the resulting 2,3-divinylcyclobutanone derivative undergoes a [3 + 3] sigmatropic rearrangement,[3,9] affording the eight-membered ring annulation product.

The scope of this [4 + 4] annulation with respect to the cyclobutenone component was examined by employing 1,3-cyclo-

hexadiene as a convenient, reactive ketenophile (Table I). The requisite cyclobutenones **3**, **4**,[11a] and **5** were prepared in 57–88% yield from the β-ethoxycyclobutenones **1**[11a] and **2**[11b] by reaction with the appropriate alkyllithium reagent, followed by hydrolysis with 10% HCl (eq 1). [4 + 4] annulations were achieved by

1, R^1 = H
2, R^1 = CH$_3$

3, R^1 = H; R^2 = CH$_3$
4, R^1 = H; R^2 = n-Bu
5, R^1 = R^2 = CH$_3$

(1)
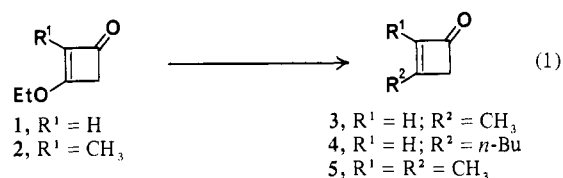
heating a solution of the cyclobutenone and 5 equiv of 1,3-cyclohexadiene in benzene or toluene in a Pyrex tube sealed with a threaded Teflon cap. Thus, reaction of 1,3-cyclohexadiene with the enone **5** at 120 °C for 4 days provided the eight-membered ring annulation product **8** in 81% yield.[12] Addition of the same diene to cyclobutenones **3** (80 °C, 65 h) and **4** (toluene, 160 °C,

(6) For a review, see: Marvell, E. N. "Thermal Electrocyclic Reactions"; Academic Press: New York, 1980; pp 124–190.

(7) For previous examples of vinylketene [2 + 2] cycloadditions, see: (a) Payne, G. B. *J. Org. Chem.* **1966**, *31*, 718. (b) Rey, M.; Roberts, S.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 417. (c) Rey, M.; Dunkelblum, E.; Allain, R.; Dreiding, A. S. *Ibid.* **1970**, *53*, 2159. (d) England, D. C.; Krespan, C. G. *J. Org. Chem.* **1970**, *35*, 3308. (e) Hickmott, P. W.; Miles, G. J.; Sheppard, G.; Urbani, R.; Yoxall, C. T. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1514. (f) Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 500. (g) Ficini, J.; Falou, S.; d'Angelo, J. *Tetrahedron Lett.* **1977**, 1931. (h) Holder, R. W.; Freiman, H. S.; Stefanchik, M. F. *J. Org. Chem.* **1976**, *41*, 3303. (i) Wuest, J. D. *Tetrahedron* **1980**, *36*, 2291. (j) Dötz, K. H.; Trenkle, B.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 287. (k) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 451.

(8) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943.

(9) This Cope rearrangement is facilitated by relief of steric strain in the cyclobutanone ring and by the accelerating effect of the carbonyl substituent.[10a,b] For examples of *alkoxy*-accelerated[10c] divinylcyclobutane rearrangements, see: (a) Kahn, M. *Tetrahedron Lett.* **1980**, 4547. (b) Levine, S. G.; McDaniel, R. L. *J. Org. Chem.* **1981**, *46*, 2199. (c) Gadwood, P. C.; Lett, R. M. *Ibid.* **1982**, *47*, 2268.

(10) (a) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (b) Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983, 6984. (c) Evans, D. A.; Golob, A. M. *Ibid.* **1975**, *97*, 4765.

(11) Ketones **1** and **2** were prepared in 48% and 75% yield, respectively, by the reaction of ketene with ethoxyacetylene and 1-ethoxypropyne by using a modification of the general method of the following: (a) Wasserman, H. H.; Piper, J. U.; Dehmlow, E. V. *J. Org. Chem.* **1973**, *38*, 1451. (b) Ficini, J.; Claeys, M.; Depezay, J. C. *Tetrahedron Lett.* **1973**, 3357. (c) Ficini, J.; Genet, J. P. *Ibid* **1975**, 2633.

20 h) afforded in each case the expected bicyclo[4.2.2]decadienone as major product. Unfortunately, annulation employing the less stable and ketenophilic dienes isoprene and (*E*)-1,3-pentadiene proved unsuccessful. No reaction was detected at 80–120 °C in these cases, and at higher temperatures dimerization of the conjugated dienes intervened.

An alternative version of the [4 + 4] annulation involves generation of the intermediate vinylketenes by the triethyl-amine-promoted 1,4-dehydrochlorination of α,β-unsaturated acid chlorides.[13] In some cases it is possible to effect ketene generation, [2 + 2] cycloaddition, and [3,3] sigmatropic rearrangement in a single step, while other annulations are best accomplished via the isolation and purification of the intermediate 2,3-divinyl-cyclobutanone derivatives. Thus, heating the vinylketene–cy-clopentadiene cycloadduct 15[8] in benzene at 120 °C for 18 h

15, R = H
17, R = CH₃

16, R = H
18, R = CH₃
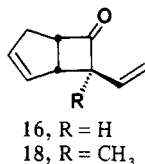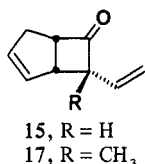
furnished bicyclo[4.2.1]nona-3,7-dien-2-one (9) in 55% yield. The identity of this annulation product was established unambiguously by its conversion to bicyclo[4.2.1]nonan-2-one[14] upon hydrogen-ation (10% Pd–C, CH₃OH, 25 °C, 4.5 h).

Similarly, rearrangement of the mixture of stereoisomeric cy-cloadducts 17 and 18 (30:70) obtained from the reaction of methylvinylketene with cyclopentadiene[7b,c,8] proceeded smoothly in toluene (160 °C, 19 h) to afford the annulation product 10 in 53% yield.[15] Both the endo- and exo-vinyl isomers in this and related systems are amenable to rearrangement. Reaction of methylvinylketene with 1,3-cyclohexadiene as described previously[8] furnished pure samples of the stereoisomeric cycloadducts 19 and

19   20   21
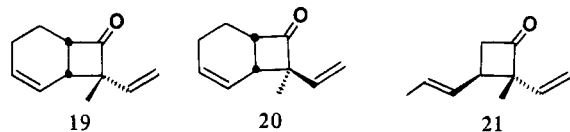
20. Separate thermolysis of these compounds then led in each case to the formation of bicyclodecadienone 11.[16] For preparative purposes the mixture of 19 and 20 (27:73) was converted to 11 (toluene, 160 °C, 19 h, 55% yield) without prior separation of isomers.

The dehydrochlorination version of the [4 + 4] annulation has been successfully applied to less ketenophilic and less stable conjugated dienes such as (*E*)-1,3-pentadiene and 1-vinylcyclo-pentene. As expected, [2 + 2] cycloaddition of methylvinylketene in these cases occurs exclusively at the less substituted double bond of the diene, resulting in the eventual formation of a single an-nulation product regioisomer. However, [4 + 4] annulation em-ploying the more sterically hindered diene 3-methylenecyclohexene proved unsuccessful under a variety of conditions. Finally, [4 +

4] annulation was also accomplished by employing chlorovinyl-ketene, which was generated by the dehydrochlorination of (*Z*)-2-chloro-2-butenoyl chloride.[7k,17]

Although in some cases the annulation proceeds in disappointing overall yield, it should be recognized that a series of three discrete reactions constitutes the total process. Furthermore, we anticipate that this [4 + 4] annulation will proceed with high stereoselectivity, as a consequence of the stereospecific nature of each of the pericyclic reactions that comprise the overall method. Further studies are underway in our laboratory to confirm this prediction, to develop more efficient versions of the annulation, and to dem-onstrate its utility in the synthesis of natural products.

Supplementary Material Available: Spectroscopic data for all new compounds (6 pages). Ordering information is given on any current masthead page.

(17) Prepared in 50% overall yield from crotonic acid via treatment with (a) Cl₂ in CS₂, 25 °C for 6 h, (b) pyridine at 115 °C for 3 h, and finally (c) SOCl₂, 90 °C, 1.5 h.

Stabilization of Dimercury through Coordination to Platinum Cluster Units

Alberto Albinati

*Istituto di Chimica Farmaceutica
Università di Milano, I-20131 Milano, Italy*

Alfred Moor, Paul S. Pregosin, and Luigi M. Venanzi*

*Laboratorium für Anorganische Chemie
ETH-Zürich, CH-8092 Zürich, Switzerland*

Although the chemistry of Hg₂²⁺ has been extensively studied, we are unaware of reports relating to the existence of the Hg₂ moiety in a molecular compound. In the course of our studies on tri- and tetranuclear platinum clusters[1,2] we observed that they reacted with metallic mercury giving deep blue-green or blue solutions from which mixed platinum–mercury clusters were isolated.

Thus, reaction of a solution of [Pt₃(μ₂-CO)₃(PPh-*i*-Pr₂)₃], 1,[1] with metallic mercury gave a blue-green solution from which dark violet crystals of [Pt₃Hg(CO)₃(PPh-*i*-Pr₂)₃]₂, 2, could be obtained.

The X-ray structure of 2 was determined.[3] The molecule, shown schematically in Figure 1, consists of *two* triangular {Pt₃(μ₂-CO)₃(PPh-*i*-Pr₂)₃} units *each capped by a mercury atom*, these two units being joined through the mercury atoms, which

(1) Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* 1981, *48*, 153.

(2) Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* 1982, *61*, 135.

(3) Crystals of 2 were obtained from acetone and are air stable. A crystal of approximate dimensions 0.25 × 0.30 × 0.20 mm was chosen for the data collection. Compound 2 ([C₇₈H₁₁₄Hg₂Pt₆P₆O₆],, M_r 2905.34) crystallizes in the triclinic space group $P\bar{1}$, with a = 12.162 (3) Å, b = 13.712 (2) Å, c = 14.730 (4) Å, α = 93.30 (2)°, β = 93.82 (2), γ = 96.59 (1)° (least-squares-refined values obtained from 23 high-angle reflections measured on an automatic diffractometer), Z = 2, V = 2429.5 (4) Å³, ρ_c = 2.026 g cm⁻³. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature up to $2\theta_{max} \leq 50.0°$ (Mo Kα graphite monochromated radiation) with an $\omega/2\theta$ scan. The scan speed was kept constant (4° min⁻¹) with a variable scan width (according to θ = 0.90 + 0.35 tan θ); background was measured at each side of the peaks for half the time of the scan. A total of 8560 independent reflections were collected, of which 6588 were considered as observed (having $I_{net} \geq 3\sigma(I)$) and subsequently used. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares analysis with use of anisotropic thermal factors for the Hg, Pt, and P atoms and isotropic for the others; a correction for the real part of the anomalous dispersion has been allowed for. Scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. IV. The present conventional agreement factor is 0.076 (for the observed reflections).

(12) Isolated yields of purified products. Annulation product 13 could only be obtained in ca. 80% purity; 8 could only be obtained in ca. 90% purity in multigram large-scale runs but could be obtained pure in smaller scale runs. Infrared, 250-MHz ¹H NMR, ¹³C NMR, and high-resolution mass spectral data were fully consistent with the assigned structures (see supplementary material).

(13) See ref 7a–c,e,h,i,k, 8 and the following; (a) Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Jpn.* 1967, *40*, 2686. (b) Iwakura, Y.; Toda, F.; Iwata, R.; Torii, Y. *Ibid.* 1969, *42*, 841. (c) Wuest, J. D.; Madonik, A. M.; Gordon, D. C. *J. Org. Chem.* 1977, *42*, 2111. (d) Danheiser, R. L.; Sard, H. *Ibid.* 1980, *45*, 4810. (e) Mohmand, S.; Hirabayashi, T.; Bock, H. *Chem. Ber.* 1981, *114*, 2609.

(14) Mp 90–93.5 °C, semicarbazone mp 204–205 °C; (lit. mp 92–93 °C, semicarbazone mp 206 °C: Sadlo, H.; Kraus, W. *Tetrahedron* 1978, *34*, 1965.

(15) Subsequent to the completion of this investigation, a report appeared by Dreiding and co-workers describing the preparation of 10 (and several related bicyclo[4.2.1]nonadienones) by an identical route; see ref 7k.

(16) The transformation of the exo-vinyl isomer 20 to 11 most likely proceeds via the diradical-mediated epimerization[3e] of 20 to 19.